Kinetic, mechanistic and spectral investigation of ruthenium(III) catalysed oxidation of atenolol by alkaline diperiodatonickelate(IV) (stopped flow technique)

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The kinetics of ruthenium(III) catalysed oxidation of atenolol by diperiodatonickelate(IV) (DPN) in alkaline medium at a constant ionic strength of 1.0 mol dm^{-3} has been studied spectrophotometrically using a rapid kinetic accessory. The reaction exhibits 1:1 stoichiometry (DPN:atenolol). The reaction shows first order dependence on [DPN] and [Ruthenium(III)] and apparent less than unit order dependence each in atenolol and alkali concentrations. Addition of periodate has no effect on the rate of reaction. Effect of added products, ionic strength and dielectric constant of the reaction medium have been investigated. The main products were identified by IR, NMR, fluorimetry and mass spectral studies. The results suggest the formation of a complex between the atenolol and ruthenium(III) species which reacts with one mole of diperiodatonickelate(IV) species in a rate determining step, resulting in the formation of a free radical, which in a subsequent fast step yields the products. The reaction constants involved in the mechanism were evaluated. The activation parameters were computed with respect to the slow step of the mechanism and discussed.

KEY WORDS: atenolol; diperiodatonickelate(IV); ruthenium (III); catalysis.

1. Introduction

The use of diperiodatonickelate(IV) (DPN) as an oxidant in alkaline medium is new and restricted to a few cases [1–6] due to the fact of its limited solubility and stability in aqueous medium. Reduction of nickel(IV) complexes have been received a considerable attention in order to understand, the nature of intermediate oxidation states of nickel such as nickel(III). Indeed, stable nickel(III) complexes are known [7–9]. Moreover, when nickel(IV) periodate is oxidant, it needs to be known which of the species is the active form of oxidant, since multiple equilibria between the different nickel(IV) species are involved.

4-(2-hydroxy-3-isopropylaminopropoxy)phenylacetamide commercially known as atenolol, a β-adrenoreceptor blocking agent is used as antihypertensive drug [10]. It is also used for anti-angina treatment to relieve symptoms, improve tolerance and as an anti-arrhythmic to regulate heartbeat and infections. It is also used in management of alcohol withdrawal, in anxiety states, migraine prophylaxis, hyperthyroidism and tremor.

In earlier reports [4–7] on DPN oxidation, periodate had a retarding effect and order in the [OH^-] was found to be less than unity in almost all the reactions and monoperiodatonickelate(IV) (MPN), is considered to be the active species. However, in the present study, we have observed different kinetic observations and deprotonated form of DPN is found to be active form of the oxidant. Literature survey reveals that there are no reports on the catalysis of oxidative mechanism of atenolol by any oxidant.

Ruthenium(III) acts as an efficient catalyst in many redox reactions particularly in an alkaline medium [11]. The catalysis mechanism can be quite complicated due to the formation of different intermediate complexes, free radicals and different oxidation states of ruthenium. The uncatalysed reaction between atenolol and nickel(IV) in an alkaline medium has been studied previously [12]. A microscopic amount of ruthenium(III) is sufficient to catalyse the reaction and a variety of mechanisms are possible. Herein we describe the results of the title reaction in order to determine the active oxidant species, reductant, catalyst species, in such media and on the basis of kinetic and spectral results to arrive at a plausible mechanism.

2. Experimental

2.1. Materials

All chemicals used were of reagent grade. Solution of atenolol (M/s. S.S. Antibiotics Pvt. Ltd, Aurangabad, India) was prepared by dissolving appropriate amount

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of recrystalised sample in double distilled water. The solid complex nickel(IV) periodate was prepared by known method [13]. Aqueous solution of DPN was obtained by dissolving the solid complex in 1.0 cmol dm^{-3} KOH solution. The Ni(IV) in alkaline solution was estimated gravimetrically [14] after reducing it to Ni(II) and precipitating Ni(II) as its dimethyl glyoxime complex. Periodate solution was prepared by weighing out the required amount of a sample in hot water and was used after keeping for 24 h. Its concentration was ascertained iodometrically [15] at neutral pH maintained by a phosphate buffer. Ni(II) solution was prepared from nickel sulphate (Fischer). Potassium hydroxide and potassium nitrate,(BDH,AR) were employed to maintain required alkalinity and ionic strength respectively.

The Ru(III) solution was prepared by dissolving a known weight of $RuCl_3$ (S.D. fine chem.) in HCl (0.20 mol dm^{-3}). Hg was added to the Ru(III) solution to reduce any Ru(IV) formed during the preparation of the Ru(III) stock solution which was set aside for 24 h. The Ru(III) concentration was then assayed by EDTA titration [16].

Since, periodate is present in an excess in the DPN complex, the possibility of atenolol oxidation by periodate in presence of catalyst in aqueous alkaline medium has been tested. It was found that the reaction is much slower than the title reaction.

2.2. Kinetic procedure

Kinetic runs were followed under *pseudo*-first order conditions with the atenolol concentration in excess over that of the oxidant at 25 ± 0.1 °C, unless otherwise stated. The reaction was initiated by mixing thermally equilibrated solutions of DPN and atenolol, which also contained a definite quantity of Ru(III), KOH, KNO_3 and IO_4^-. Here the total concentration of hydroxide ion was calculated considering the KOH in DPN as well as the KOH additionally added. Similarly, the total metaperiodate concentration was calculated by considering the amount present in the DPN solution and that additionally added. The course of reaction was followed by measuring the absorbance of unreacted DPN in the reaction mixture in a 1 cm quartz cell located in the thermostatted compartment of a Peltier Accessory (temperature control) attached Varian CARY 50 Bio UV–Vis spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12) at its maximum absorption wavelength of 410 nm as a function of time. Earlier it was verified that there is negligible interference from other species present in the reaction mixture at this wavelength. The obedience of Beer's law by DPN at 410 nm was verified earlier and the molar absorbance coefficient, 'ε' was found to be 7500 ± 375 dm^3 mol^{-1} cm^{-1} at this wavelength. The first order rate constants, k_C were obtained from the plots of log (absorbance) versus time. The plots were linear up to about 85% completion of the reaction and the rate constants were reproducible within ± 5%.

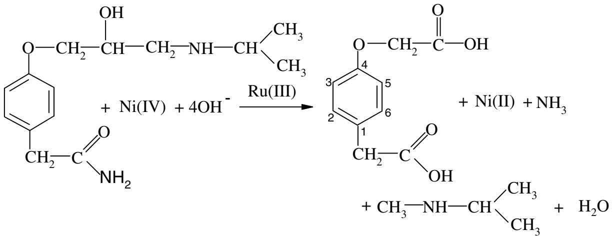
In view of the modest concentration of alkali used in the reaction medium, attention was also directed to the effect of the reaction vessel surface on the kinetics. Use of polythene/acrylic wares and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on reaction rates.

Kinetic runs were also carried out in an N_2 atmosphere in order to understand the effect of dissolved oxygen on the rate of reaction. No significant difference in the results was obtained under a N_2 atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in the basic medium, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rates, however, fresh solutions were nevertheless used while carrying out the kinetic study.

3. Results

3.1. Stoichiometry and product analysis

Different sets of reaction mixtures containing different concentrations of atenolol and DPN with a constant amount of ruthenium(III) at constant ionic strength and alkali were kept for ca. 2 h. at 25 ± 0.1 °C in a N_2 atmosphere. When [DPN] was higher than [atenolol], the unreacted DPN was found by measuring the absorbance at 410 nm. The results indicated that one mole of DPN consumed one mole of atenolol as shown in equation (1).



(1)

The reaction product, 4-carboxy methoxy phenyl acetic acid was extracted with ether and recrystallised from aqueous alcohol and the purity was checked by HPLC. This is identified as 4-carboxy methoxy phenyl acetic acid by its I.R. spectrum, which showed a band at (υ) 1690 cm^{-1} due to > C=O stretching of acid and a broad band at 2845 cm^{-1} due to O–H stretching. 4-carboxy methoxy phenyl acetic acid was further characterised by ^{1}H NMR spectrum (DMSO), showed a singlet at 9.6 δ due to two carboxylic OH, a doublet ($J = 9$ Hz) at 6.94 δ due to C_3– and C_5– protons, another doublet ($J = 9$ Hz) at 7.20 δ due to C_2– and C_6– protons, a singlet at 3.53 δ due to methylene protons of ph–CH_2– and another singlet at 4.58 δ due to methylene protons of ph–O–CH_2– respectively and mass spectra ESI technique (solvents:acetonitrile + water + ammonium acetate) ($M^+ + 17$) (ammoniated) 228 and (M^+) m/z 211. Ammonia was identified by using Nessler's reagent [17]. Ni(II) was identified by its dimethyl glyoxime complex [14].

N-Isopropylmethylamine which is soluble in water was identified by spot test [18]. It was observed that the 4-carboxy methoxy phenyl acetic acid and *N*-Isopropylmethylamine do not undergo further oxidation under the present kinetic conditions.

3.2. Spectrofluorimetric studies

The fluorescence study was carried out in methanol as solvent by our proper study for good dissolution of pure and product compound. There was no interference of the solvent methanol seen in the fluorescent study. We have taken the fluorescence study of pure compound atenolol and also for the product of the reaction of atenolol with DPN in presence of ruthenium(III) catalyst in aqueous alkaline medium. The excitation for the atenolol was observed at 370 nm and the emission was found at 411 nm with intensity 106. The excitation of the product was observed at 370 nm and the emission was found at 416 nm with the considerable decrease in the fluorescent intensity to 36.62, which is due to quenching.

Regression analysis of experimental data to obtain the regression coefficient r and standard deviation S of points from the regression line was performed using a Pentium-III personnel computer.

3.3. Reaction order

As the diperiodatonickelate(IV) oxidation of atenolol in alkaline medium proceeds with a measurable rate in the absence of ruthenium(III), the catalysed reaction is understood to occur in parallel paths with contributions from both the catalysed and uncatalysed paths. Thus, the total rate constant (k_T) is equal to the sum of the rate constants of the catalysed (k_C) and uncatalysed (k_U) reactions, so $k_C = k_T - k_U$. Hence the reaction orders have been determined from the slopes of log k_C versus log concentration plots by varying the concentrations of atenolol, Ru(III) and alkali in turn while keeping the others constant.

The concentration of diperiodatonickelate(IV) was varied in the range, 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} at fixed [atenolol], [Ru(III)], [OH^-] and ionic strength. The non-variation in the pseudo-first order rate constants at various concentrations of DPN indicates the order in [DPN] as unity (Table 1). This was also confirmed from the linearity of plots of log (Absorbance) versus time (r >0.9994, S ≤0.026) up to 85% completion of the reaction (Figure 1). The substrate, atenolol was varied in the range of 1.0×10^{-4} to

Table 1
Effect of variation of [DPN], [ATN], [Ru(III)], [OH^-] and [IO_4^-] and on Ru(III) catalysed oxidation of atenolol by DPN in aqueous alkaline medium at 25 °C and I = 1.0 mol dm^{-3}

[DPN] × 10^4 (mol dm^{-3})	[ATN] × 10^3 (mol dm^{-3})	[Ru(III)] × 10^6 (mol dm^{-3})	[OH^-] (mol dm^{-3})	[IO_4^-] × 10^4 (mol dm^3)	$k_T \times 10^2$ (s^{-1})	$k_U \times 10^3$ (s^{-1})	$k_C \times 10^2$ (s^{-1})	
							Expt	Calc.
0.1	1.0	1.0	0.2	5.0	3.42	5.61	2.85	2.95
0.3	1.0	1.0	0.2	5.0	3.43	5.64	2.86	2.95
0.6	1.0	1.0	0.2	5.0	3.41	5.63	2.84	2.95
0.8	1.0	1.0	0.2	5.0	3.44	5.62	2.87	2.95
1.0	1.0	1.0	0.2	5.0	3.40	5.64	2.84	2.95
1.0	0.1	1.0	0.2	5.0	1.13	5.58	0.57	0.57
1.0	0.3	1.0	0.2	5.0	1.93	5.57	1.37	1.41
1.0	0.6	1.0	0.2	5.0	2.95	5.59	2.39	2.25
1.0	0.8	1.0	0.2	5.0	3.28	5.60	2.72	2.65
1.0	1.0	1.0	0.2	5.0	3.40	5.64	2.84	2.95
1.0	1.0	0.1	0.2	5.0	0.83	5.64	0.26	0.29
1.0	1.0	0.3	0.2	5.0	1.43	5.64	0.86	0.88
1.0	1.0	0.6	0.2	5.0	2.25	5.64	1.68	1.77
1.0	1.0	0.8	0.2	5.0	2.85	5.64	2.28	2.24
1.0	1.0	1.0	0.2	5.0	3.40	5.64	2.84	2.95
1.0	1.0	1.0	0.1	5.0	2.42	3.04	2.11	2.20
1.0	1.0	1.0	0.2	5.0	3.40	5.64	2.84	2.95
1.0	1.0	1.0	0.4	5.0	4.32	8.20	3.50	3.57
1.0	1.0	1.0	0.8	5.0	5.03	13.0	3.73	3.98
1.0	1.0	1.0	1.0	5.0	5.37	14.0	3.97	4.08
1.0	1.0	1.0	0.2	1.0	3.42	5.59	2.86	–
1.0	1.0	1.0	0.2	2.0	3.44	5.58	2.88	–
1.0	1.0	1.0	0.2	5.0	3.40	5.64	2.84	–
1.0	1.0	1.0	0.2	8.0	3.41	5.62	2.85	–
1.0	1.0	1.0	0.2	10	3.43	5.63	2.86	–

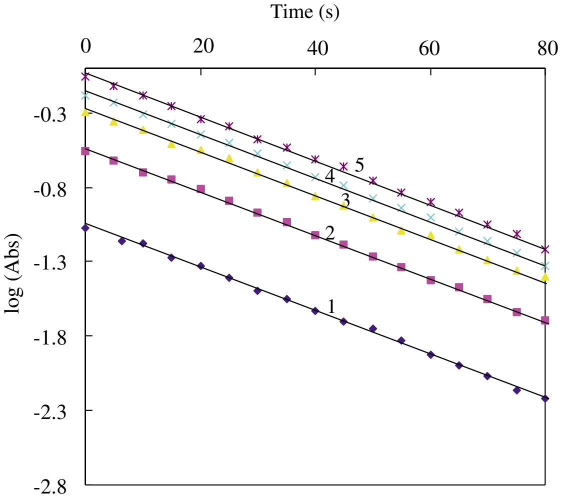


Figure 1. First order plots of Ru(III) catalysed oxidation of atenolol by aqueous alkaline Diperiodateonickelate(IV) at 25 °C. [DPN] × 10^5 (mol dm^{-3}); (1) 1.0 (2) 3.0 (3) 6.0 (4) 8.0 (5) 10.

1.0×10^{-3} mol dm^{-3} at 25 °C keeping all other reactants concentrations including ruthenium(III) catalyst and conditions constant. The k_{obs} values were increased with increase in concentration of atenolol indicating an apparent less than unit order dependence on [atenolol] (Table 1). The ruthenium(III) concentrations was varied from 1.0×10^{-7} to 1.0×10^{-6} mol dm^{-3} range, at constant concentration of diperiodatonickelate(IV), atenolol, alkali and ionic strength. The order in [Ru(III)] was found to be unity (Table 1) from the linearity of the plots of log k_{obs} versus log [Ru(III)] ($r >0.9997$, $S \leq 0.022$). The effect of [alkali] on the rate of reaction was studied at constant concentrations of atenolol, diperiodatonickelate(IV), ruthenium(III) and a constant ionic strength at 1.0 mol dm^{-3}. The rate constants increased with increase in [alkali] (Table 1). The effect of [IO_4^-] was observed by varying the concentration from 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} at constant concentrations of diperiodatonickelate(IV), atenolol, ruthenium(III), alkali and ionic strength. It was found that the added periodate has no effect on the rate of reaction (Table 1).

3.4. Effect of ionic strength and solvent polarity

The effect of ionic strength was studied by varying the [KNO_3] in the reaction mixture. The ionic strength of the reaction medium was varied from 0.2 to 2.0 mol dm^{-3} at constant [DPN], [atenolol], [Ruthenium(III)], [IO_4^-] and [alkali]. It was found that the ionic strength has negligible effect on the rate of reaction. The relative permittivity (ε_T) effect was studied by varying the *t*-butyl alcohol-water content in the reaction mixture with all other conditions being constant, that is including Ru(III) catalyst. Attempts to measure the relative permittivities of the mixture of *t*-butyl alcohol–water were not successful. However, they were computed from the values of pure liquids [19]. There was no reaction of the solvent with the oxidant under the experimental conditions used. It was found that change in dielectric constant has negligible effect on the rate of the reaction.

3.5. Effect of initially added products

The initially added products, such as Ni(II) and 4-carboxy methoxy phenyl acetic acid, did not have any significant effect on the rate of the reaction.

3.6. Test for free radicals

To test the intervention of free radicals, the reaction mixture was mixed with acrylonitrile monomer and kept for 24 h under nitrogen atmosphere. On dilution with methanol, white precipitate of polymer was formed, indicating the presence of intervention of free radicals in the reaction. The blank experiment of either DPN and Ruthenium(III) or atenolol and Ruthenium(III) alone with acrylonitrile did not induce polymerisation under the same condition as those induce with reaction mixtures. Initially added acrylonitrile decreases the rate indicating the free radical intervention, which is the case in earlier work [20].

3.7. Effect of temperature

The rate of the reaction was measured at four different temperatures, with varying [Atenolol], keeping other conditions constant. The rate was found to increase with increase in temperature. The rate constants k, of the slow step of Scheme 1 were obtained from the slopes and intercepts of the plots of [Ru(III)]/k_C versus 1/[OH^-] ($r > 0.9986$, $S \leq 0.041$) and [Ru(III)]/k_C versus 1/[atenolol] ($r > 0.9994$, $S \leq 0.050$). The values of $k \times 10^4$ (dm^3 mol^{-1} s^{-1}) were 8.42, 8.95, 9.65 and 10.43 at 25, 30, 35 and 40 °C, respectively. The activation parameters were evaluated from the Arrhenius plot of log k versus 1/T ($r > 0.9976$, $S \leq 0.035$). The values of Ea, ΔH, ΔS and ΔG were obtained and are given in Table 2.

4. Discussion

The water soluble [8,9] Ni(IV) periodate complex is reported [21–24] to be $[Ni(HIO_6)_2(OH)_2]^{6-}$. Although, periodate is involved in multiple equilibria (I–III)

$$H_5IO_6 \overset{K_1}{\rightleftharpoons} H_4IO_6^- + H^+, \quad K_1 = 5.1 \times 10^{-4} \qquad (I)$$

$$H_4IO_6^- \overset{K_2}{\rightleftharpoons} H_3IO_6^{2-} + H^+, \quad K_2 = 4.9 \times 10^{-9} \qquad (II)$$

$$H_3IO_6^{2-} \overset{K_3}{\rightleftharpoons} H_2IO_6^{3-} + H^+, \quad K_3 = 5.1 \times 10^{-12} \qquad (III)$$

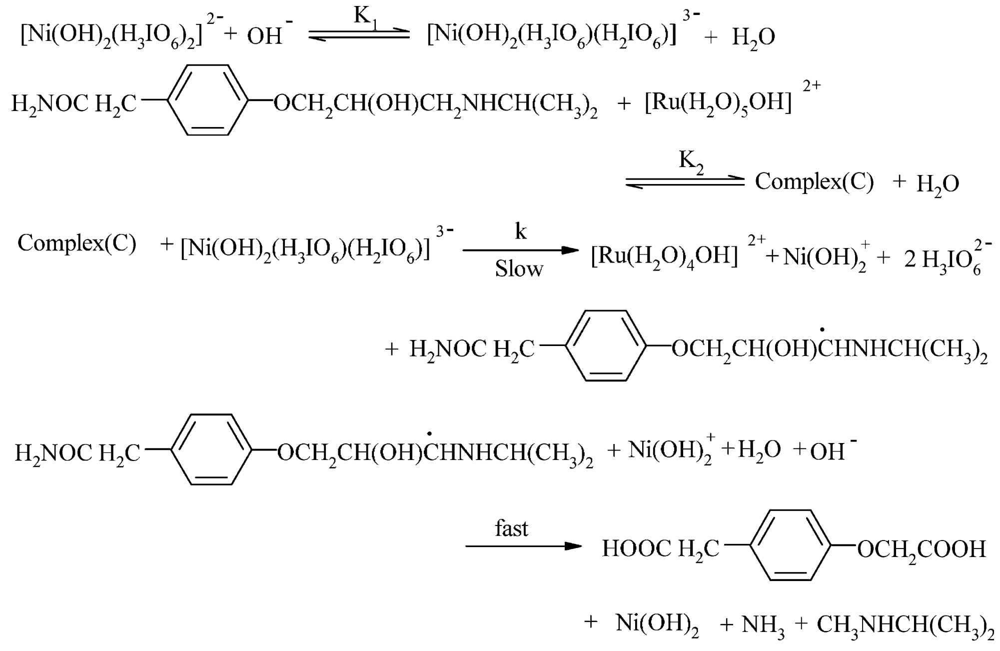
which prevail to varying extends depending on the pH employed, under condition of high pH 13.3 of the study the form which predominates is understood to be the species, $H_3IO_6^{2-}$ (not as HIO_6^{4-} present in the Ni(IV) complex [4–6,22,25]). Periodic acid (H_5IO_6) exists in acid medium and also as $H_4IO_6^-$ around a pH of 7. Thus, under the conditions employed in the alkaline medium, the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerise. Hence at the pH employed in the study, the Ni(IV) periodate complex exists as DPN, $[Ni(H_3IO_6)_2(OH)_2]^{2-}$, a conclusion also supported by earlier work [4–6,21–22].

It is interesting to identify the probable ruthenium(III) chloride species in alkaline media. Electronic spectral studies [26] have confirmed that ruthenium(III) chloride exists in hydrated form as $[Ru(H_2O)_6]^{3+}$. In the present study it is quite probable that the $[Ru(H_2O)_5OH]^{2+}$ species might assume the general form $[Ru^{III}(OH)_x]^{3-x}$. The x value would always be less than six because there are no definite reports of any hexahydroxy ruthenium species. The reminder of the coordination sphere will be filled by water molecules. Hence, under the conditions $[OH^-] >> [Ru^{III}]$, ruthenium(III) is mostly present [27] as the hydroxylated species, $[Ru(H_2O)_5OH]^{2+}$.

The reaction between DPN and atenolol in alkaline medium in the presence of ruthenium(III) has a 1:1 stoichiometry of oxidant to reductant with first order dependence on both [DPN] and [Ruthenium(III)],the apparent order of less than unity in $[OH^-]$ and [atenolol]. In most of the reports [4–7] on DPN oxidation, periodate had a retarding effect and order in the $[OH^-]$ was found to be less than unity and monoperiodatonickelate(IV) (MPN), is considered to be the active species. However, in the present kinetic study, different kinetic observations have been obtained i.e., periodate has totally no effect on the rate of reaction. Accordingly DPN itself is considered to be the active species of oxidant. The results indicate that the DPN combines with alkali to form a deprotonated form of DPN in a prior equilibrium step, which is also supported by the observed fractional order in $[OH^-]$. Atenolol reacts with ruthenium(III) species to form a complex (C) which reacts with one mole of deprotonated form of DPN in a slow step to give a free radical derived from atenolol and nickel(III) intermediate species with regeneration of catalyst, ruthenium(III). The existence of such free radical was mentioned in literature [28]. K_2 in the equilibrium constant comparing the equilibrium to bind atenolol to ruthenium(III). This free radical reacts with nickel(III) species in a fast step to yield the products as given in Scheme 1. The evidence for nickel (III) formation is in accordance with earlier work [29].

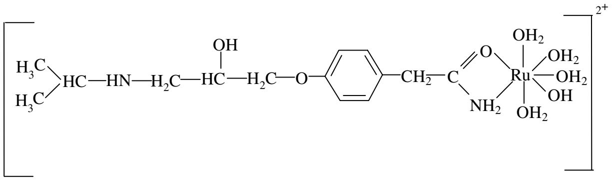
Spectral evidence for such a catalyst-substrate complex was obtained from the UV-Vis spectra of atenolol and mixture of ruthenium(III) and atenolol. A hypsochromic shift, λ_{max}, of ca. 5 nm from 343 to 338 nm is observed together with hyperchromicity at 338 nm. Such complex between a substrate and a catalyst has been observed in other studies [30].

The thermodynamic quantities for the second equilibrium step in Scheme 1 can be evaluated as follows: The substrate concentration (as in Table 1) was varied at four different temperatures and the value of K_2 was determined at each temperature. The values of $K_2 \times 10^3$ (dm^3 mol^{-1}) were obtained as 1.15, 1.77, 2.58 and 3.54 at 25, 30, 35 and 40 °C, respectively. A vant Hoff's plot was made for the



Scheme 1.

Probable structure of the complex (C) is given by



Scheme 2.

variation of K_2 with temperature [i.e., log K_2 versus $1/T$ ($r > 0.9985$, $S \leq 0.036$)] and the values of the enthalpy of reaction, ΔH, entropy of reaction, ΔS, and free energy of reaction, ΔG, were calculated as 58.1 ± 2.6 kJ mol^{-1}, 253 ± 12 J K^{-1} mol^{-1} and −19.4 ± 1.0 kJ mol^{-1}, respectively. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step are fairly slow and involves high activation energy [31].

In the presence of catalyst, the reaction is understood to occur in parallel paths with contribution from the uncatalysed and catalysed paths. Thus the total rate constant (k_T) is equal to the sum of the rate constants of the catalysed (k_C) and uncatalysed (k_U) reations. It is interesting to note that in case of uncatalysed reaction, the order with respect to atenolol is zero [12].

Scheme 1 leads to rate low [2] as follows

$$\text{Rate}_{\text{Cat}} = \text{Rate}_{\text{Total}} - \text{Rate}_{\text{Uncat}}$$

where the right hand side represents the catalysed path.

$$\text{Rate}_{\text{Cat}} = -\frac{d[\text{Ni(IV)}]}{dt} = \frac{kK_1K_2[\text{ATN}][\text{Ru(III)}][\text{OH}^-][\text{Ni(IV)}]}{1+K_1[\text{OH}^-]+K_2[\text{ATN}]+K_1K_2[\text{OH}^-][\text{ATN}]} \tag{2}$$

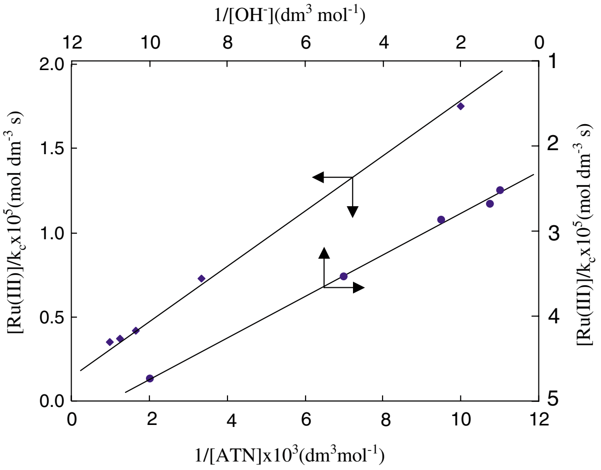


Figure 2. Verification of rate law [3] (conditions as in Table I).

The terms (1+ K_1[Ni(IV)]) and (1+ K_2[Ru(III)]) should be in the denominator of equation (2). But in view of low concentration of Ni(IV) and ruthenium(III) used, they approximate to unity. Thus the above equation (2) can be rearranged to the following form, which is used for the verification of the rate law.

In terms of rate constants,

$$\frac{\text{Rate}}{[\text{Ni(IV)}]} = K_C = K_T - K_U = \frac{kK_1K_2[\text{ATN}][\text{Ru(III)}][\text{OH}^-]}{1+K_1[\text{OH}^-]+K_2[\text{ATN}]+K_1K_2[\text{OH}^-][\text{ATN}]} \tag{3}$$

Equation (3) can be rearranged to equation (4), which is suitable for verification.

$$\frac{[\text{Ru(III)}]}{K_C} = \frac{1}{kK_1K_2[\text{ATN}][\text{OH}^-]} + \frac{1}{kK_2[\text{ATN}]} + \frac{1}{kK_1[\text{OH}^-]} + \frac{1}{k} \tag{4}$$

Table 2

Thermodynamic activation parameters for the Ru(III) catalysed oxidation of atenolol by Diperiodateonickelate(IV) in alkaline medium with respect to the slow step of Scheme 1

	Temp. (K)	$k \times 10^4$ (dm^3 mol^{-1} s^{-1})
(a) Effect of temperature		
298	8.42	
303	8.95	
308	9.65	
313	10.43	
Parameters	Catalysed reaction	Uncatalysed reaction [12]
(b) Activation parameters		
E_a (kJ mol^{-1})	11.2 ± 0.6	43.8 ± 2.5
log A	6.9 ± 0.3	6.0 ± 0.3
ΔH (kJ mol^{-1})	8.6 ± 0.6	41.2 ± 2.0
ΔS (JK^{-1} mol^{-1})	−121.7 ± 6.0	−138 ± 7.0
ΔG (kJ mol^{-1})	46 ± 2	84 ± 4

According to equation (4), the plots of [Ru(III)]/k_C versus 1/[ATN] and [Ru(III)]/k_C versus1/[OH^-] ($r > 0.9994$, $S \leq 0.050$ and $r > 0.9986$, $S \leq 0.041$) are linear with an intercept supporting the Ru(III)-atenolol complex, and which is verified in Figure 2. From the slope and intercept of such plots, the values of K_1, K_2 and k are calculated as 9.6 ± 0.1 $dm^3\ mol^{-1}$, 1.15 ± 0.08 × $10^3\ dm^3\ mol^{-1}$ and 8.41 ± 0.3 × $10^4\ dm^3\ mol^{-1}\ s^{-1}$. The value of $K_1$is in agreement with earlier value [32]. Using these K_1, K_2 and k values, the rate constants under different experimental conditions were calculated by equation (3) and compared with experimental data. There is a good agreement between them (Table 1).

The difference in the activation parameters for the catalysed (k_C) and uncatalysed (k_U) reaction (Table 2) explains the catalytic effect on the reaction. The catalyst, Ru(III) forms the complex with atenolol which shows more reducing property than atenolol itself. Hence the catalyst, Ru(III) lowers energy of activation. The negative value of ΔS indicates that the complex (C) is more ordered than the reactants. The observed modest enthalpy of activation and higher rate constant of slow step indicate that the oxidation presumably occurs by inner-sphere mechanism. This conclusion is supported by earlier work [33].

The negligible effect of ionic strength and dielectric constant on the rate of reaction supports the proposed mechanism (Scheme 1). Spectrofluorimetric studies reveal that the fluorescence intensity is quenched, which may be due to the electron transfer reaction [34].

4. Conclusion

Among various species of Ni(IV) in alkaline medium, in earlier reports the monoperiodatonickelate(IV) (MPN) was the active species, whereas, diperiodateonickelate(IV) is considered to be the active species for the title reaction. Rate constant of slow step and other equilibrium constants involved in the mechanism are evaluated and activation parameters with respect to slow step of reaction were computed. The overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.

Appendix

$$\text{Rate}_{\text{Cat}} = \text{Rate}_{\text{Total}} - \text{Rate}_{\text{Uncat}}$$

$$\begin{aligned}\text{Rate}_{\text{Cat}} &= k[\text{C}]\left[\text{Ni(OH)}_2(\text{H}_2\text{IO}_6)(\text{H}_3\text{IO}_6)\right]^{3-} \\ &= kK_1K_2[\text{ATN}][\text{Ni(IV)}][\text{OH}^-][\text{Ru(III)}]\end{aligned} \qquad (A.1)$$

The total concentration of reductant, $[\text{ATN}]_T$ is given by

$$[\text{ATN}]_T = [\text{ATN}]_f + \text{C} = [\text{ATN}]_f(1 + \text{K}_2\text{Ru(III)})$$

Therefore,

$$[\text{ATN}]_f = \frac{[\text{ATN}]_T}{1 + K_2[\text{Ru(III)}]} \qquad (A.2)$$

Similarly,

$$[\text{Ni(IV)}]_f = \frac{[\text{Ni(IV)}]_T}{1 + K_1[\text{OH}^-]} \qquad (A.3)$$

Similarly,

$$[\text{OH}^-]_f = \frac{[\text{OH}^-]_T}{1 + K_1[\text{Ni(IV)}]} \qquad (A.4)$$

and

$$[\text{Ru(III)}]_f = \frac{[\text{Ru(III)}]_T}{1 + K_2[\text{ATN}]} \qquad (A.5)$$

Substituting (A.2),(A.3),(A.4) and (A.5) in (A.1),we get

$$\begin{aligned}\text{Rate} &= \frac{d[\text{Ni(IV)}]}{dt} \\ &= kK_1K_2[\text{ATN}][\text{Ni(IV)}][\text{OH}^-][\text{Ru(III)}] \\ &\quad /(1 + K_2[\text{Ru(III)}])(1 + K_1[\text{OH}^-]) \\ &\quad \times(1 + K_1[\text{Ni(IV)}])(1 + K_2[\text{ATN}])\end{aligned} \qquad (A.6)$$

References

[1] D.H. Macartney and A. McAuley, Inorg. Chem. 22 (1983) 2062.

[2] S. Acharya, G. Neogi, R.K. Panda and D. Ramaswamy, Int. J. Chem. Kinet. 14 (1982) 1253.

[3] A.G. Lappin, M.C. Laranjeira and O.L. Youdi, J. Chem. Soc. Dalton Trans. (1981) 721.

[4] M.A. Siddiqui, C.S. Kumar, U. Chandraiah and S. Kandlikar, Indian J. Chem. 30A (1991) 849.

[5] P.D. Pol, C.P. Kathari and S.T. Nandibewoor, Transit. Met. Chem. 28 (2003) 209.

[6] D.C. Bilehal, R.M. Kalkarni and S. T. Nandibewoor, Inorg. React. Mech. 4 (2002) 103.

[7] S. Bhattacharya, B. Saha, A. Datta and P. Banerjee, Coordin. Chem. Rev. 47 (1970) 170.

[8] R.I. Haines and A. McAulley, Coordin. Chem. Rev. 39 (1981) 77.

[9] K. Nag and A. Chakravarty, Coordin. Chem. Rev. 33 (1980) 87.

[10] M. White, A. Fourney, E. Mikes and F.H.H. Leenen, Am. J. hypertens 12 (1999) 151.

[11] N. Swarnalaxmi, V. Uma, B. Sethuram and T. Navaneeth Rao, Indian J. Chem. 26A (1987) 592 ; A.K.Kini, S.A. Farokhi and S.T. Nandibewoor, Transit. Met. Chem. 27 (2002) 532.

[12] R.M. Mulla, R.M. Kulkarni and S.T. Nandibewoor, J. Chem. Res. Suppl. (2003) 315.

[13] P. Ray in:*Inorganic Synthesis*, ed., Therald Moellar (McGraw-Hill, New York, 1957) p. 201.

[14] G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney In:*Vogel's Text Book of Quantitative Chemical Analysis 5th edn.* (ELBS Longman, Essex, UK, 1996) p. 462.

[15] G. P. Panigrahi and P.K. Misro, Indian J. Chem. 16 (1978) 201.

[16] C.S. Reddy and T. Vijaykumar, Indian J. Chem. 34 (1995) 615 ; A.G. Sykes, H. Emeleus and A.G. Sharpe, eds, In Advances in Inorganic and Radiochemistry, Vol. 10 (Academic press, New York, 1967). p.321.

[17] G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney In: *Vogel's Text Book of Quantitative Chemical Analysis 5th ed.* (ELBS Longman, Essex, UK, 1996) p. 679.

[18] F. Feigl *Spot Tests in Organic Analysis* (Elsevier Publishing companyAmsterdam, 1975) p. 250.

[19] D.R. Lide, (ed.) *CRC Hand Book of Chemistry and Physics 73rd ed.* (CRC press, London, 1993), pp. 8–51.

[20] I.M. Kolthoff, E.J. Meehan and E.M. Carr, J. Am. Chem. Soc. 75 (1953) 1439 ; A.A. Frost and R.G. Pearson, Kinetics and Mechanism (Wiley Eastern (P) Ltd., New Delhi, 1970) p. 367.

[21] G.H. Hugar and S.T. Nandibewoor, Indian J. Chem., 32A (1993) 1056.

[22] U. Chandraiah, C.P. Murthy and S. Kandlikar, Indian J. Chem. 28A (1989) 248.

[23] R.M. Kulkarni, D.C. Bilehal and S.T. Nandibewoor, J. Chem. Res (Suppl.) (2002) (M)401, (S)147.

[24] A.L. Harihar, M.R. Kembhavi and S.T. Nandibewoor, Inorg. React. Mech. 1 (1999) 145.

[25] H.G. Mukherjee, M. Bhansidar and D. Shyamali, Indian J. Chem. 23A (1984) 426.

[26] A.M. Balado, B.C. Galan and F.J.P. Martin, Anals. De. Quimica. 88 (1992) 170 ; F.A. Cotton and G. Wilkinson in Advanced Inorganic Chemistry (New York, Wiley Eastern, 1996) p. 153.

[27] D.L. Kamble and S.T. Nandibewoor, Oxidn. Commun. 21 (1998) 396 ; H.S. reddy and T.V. kumar, Indian J. Chem., 34A (1995) 615; G.A. Hiremath, P.L. Timmanagoudar and S.T. Nandibewoor, React. Kinet. Catal. Lett. 63 (1998) 403; D.L. Kamble and S.T. Nandibewoor, J. Phys. Org. Chem.11 (1998) 171; S.M. Desai, N.N. Halligudi and S.T. Nandibewoor, Transit. Met. Chem. 27 (2002) 207.

[28] D.C. Bilehal, R.M. Kulkarni and S.T. Nandibewoor, Can. J. Chem. 79 (2001) 1926.

[29] S. Bhattacharya, M. Ali, S. Gangopadhyay and P. Banerjee, J. Chem. Soc. Dalton Trans.1996) 2645 ; J.J. Zuckerman, ed., Inorganic Reactions and Methods, Vol. 15 (VCH Deerfield Beach, FL, 1986) p. 13.

[30] V. Rao and V. Jagannadham, React. Kinet Catal. Lett. 27 (1985) 239:V.A.Morab and S.T. Nandibewoor, React. Kinet. Catal. Lett. 53 (1994) 25.

[31] K.S. Rangappa, M.P. Raghavendra, D.S. Mahadevappa and D. Channagouda, J. Org. Chem., 63 (1998) 531.

[32] J.A. Khan, U. Chandraiah, B.K. Kumar and S. Kandlikar, Indian J. Chem. 29A (1990) 241.

[33] J.M. Lancaster and R.S. Murray, J. Chem. Soc. A (1971) 2755: M. Martinez, M.A. Pitarque and R.V. Eldik, J. Chem. Soc. Dalton Trans. (1996) 2665; S.A. Farokhi and S.T. Nandibewoor, Tetrahedron 59 (2003) 7595.

[34] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy* (Plenum press, New York, 1986) p. 257.